

Electronic Supplementary Information

High Electrocatalytic Activity of Self-standing Hollow NiCo₂S₄ Single Crystalline Nanorod Arrays towards Sulfide Redox Shuttles in Quantum Dot-sensitized Solar Cells

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Experimental

Synthesis of self-standing hollow NiCo₂S₄ single crystalline nanorod arrays on FTO glass substrates. The details were described as follows: FTO glass substrates were first sonicated in acetone and ethanol, and then dried by compressed air. Then, FTO glass substrate are suspended in 30 mL aqueous solution containing CoCl₂ • 6H₂O, NiCl₂ • 6H₂O and urea (35 mM). The total concentration of Co²⁺ and Ni²⁺ cations is 15 mM. After above aqueous solution are subsequently placed at 95 °C for 12 h to form metallic carbonate hydroxide precursors on FTO glass substrate, and rinsed by DI water and ethanol. The products are thermally decomposed under air atmosphere at 400 °C for 1 h with a heating rate of 5 °C min⁻¹, forming metal oxides

nanostructure. When the metallic carbonate hydroxide precursors are reacted with H₂S gas for 12 h at room temperature, and then are thermally decomposed under Ar atmosphere at 400 °C for 1 h with a heating rate of 5 °C min⁻¹, forming metal oxides-metal sulfides core-shell nanostructure. Finally, after the acid etching process to remove metal oxides, metal oxides-metal sulfide core-shell nanostructure was transformed into hollow metal sulfide nanostructure.

General Materials Characterization. The product morphologies were directly examined by scanning electron microscopy (SEM) using JEOL JSM-6700F at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) observations were carried out on a JEOL 2010 microscope operating both at 200 kV. X-ray diffraction (XRD) was performed on a Philips PW-1830 X-ray diffractometer with Cu K α irradiation ($\lambda=1.5406$ Å). The step size and scan rate are set as 0.05° and 0.025°/s, respectively. X-ray photoelectron spectroscopy (XPS) was measured on a Perkin-Elmer model PHI 5600 XPS system with a resolution of 0.3-0.5 eV from a monochromated aluminium anode X-ray source with K α radiation (1486.6 eV).

Characterization of Quantum Dot solar cells (QDSCs). QDSCs were made by sandwiching the as-prepared CEs and the photoanodes using Surlyn films (25 μ m) as the spacer. The aqueous polysulfide electrolyte is the aqueous solution of 2 M Na₂S and 2 M S. The thermally platinized FTO glass prepared by pyrolysis of H₂PtCl₆ was used as the reference CE. ZnS modified CdSe quantum dot sensitized TiO₂ film was used as the photoanode, prepared by the so-called successive ionic layer adsorption and reaction (SILAR) method.¹ The TiO₂ electrodes are composed of 100 nm dense

layer made by the spray pyrolysis of titanium diisopropoxide bis(acetylacetonate), 10 μm transparent layer made of 20 nm anatase nanoparticles, and 4 μm light scattering layer made of 400 nm TiO_2 nanoparticles. For the growth of CdSe on the TiO_2 electrode, the TiO_2 electrodes were successively immersed in two different solutions for 1 min each inside a glovebox under N_2 atmosphere: one consisting of 30 mM $\text{Cd}(\text{NO}_3)_2$ dissolved in ethanol, another of 30 mM Se^{2-} in ethanol prepared by the Grätzel's method.² Following each immersion, rinsing and drying was carried out using ethanol and N_2 gas, respectively. The processes were repeated 8 times. Then, the CdSe sensitized TiO_2 films have been coated with ZnS layer, by twice dipping alternately into 100 mM $\text{Zn}(\text{CH}_3\text{COO})_2$ and 100 mM Na_2S solutions for 1 min/dip, rinsing with the ultrapure water between dips.

The photocurrent-voltage (J - V) characteristics of QDSCs were measured using a Newport AM 1.5G solar simulator (model 91192) at the light intensity of 100 mW cm^{-2} , calibrated by a standard silicon reference cell. The active area of QDSCs was set at 0.16 cm^2 , determined by a square mask. Incident photo-to current conversion efficiency (IPCE) was measured on the basis of a Newport Apex Monochromator illuminator (model 70104). The incident photon-to-current conversion efficiency (IPCE) was measured on the basis of a Newport Apex Monochromator illuminator (model 70104). Electrochemical measurements were carried out on a CHI 660D. For electrochemical impedance spectroscopy (EIS) measurement, the symmetrical cells based on identical CEs (under dark) were carried out at zero V with the AC amplitude

of 10 mV and the testing frequency range was set from 1000 kHz to 100 mHz. The scan rate was set at 5 mV s⁻¹ in the Tafel polarization measurement.

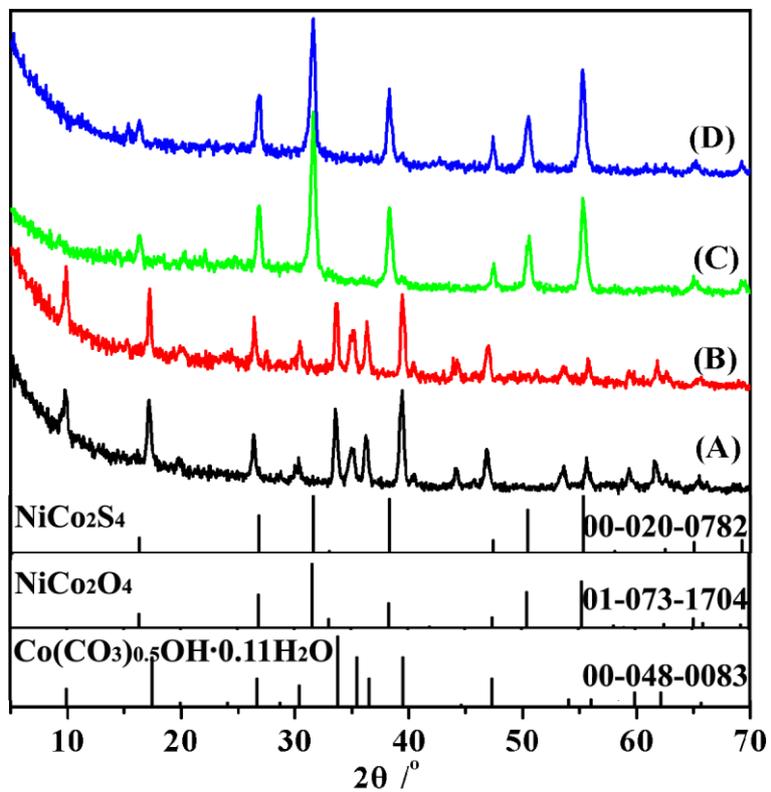


Figure SI-1. XRD patterns of the products formed after Step I (A), II (B), III (C), and IV (D) of scheme 1.

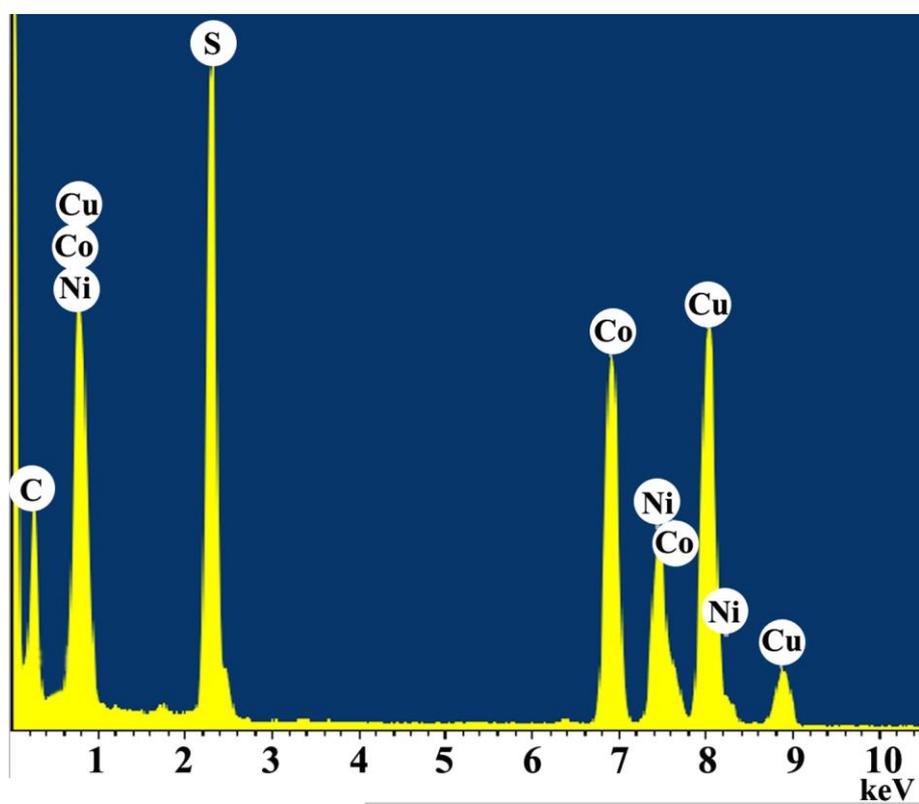


Figure SI-2. EDX spectrum of hollow NiCo_2S_4 single crystalline nanorod. Cu element is raised from the Cu mesh, and C element comes from carbon film on Cu mesh.

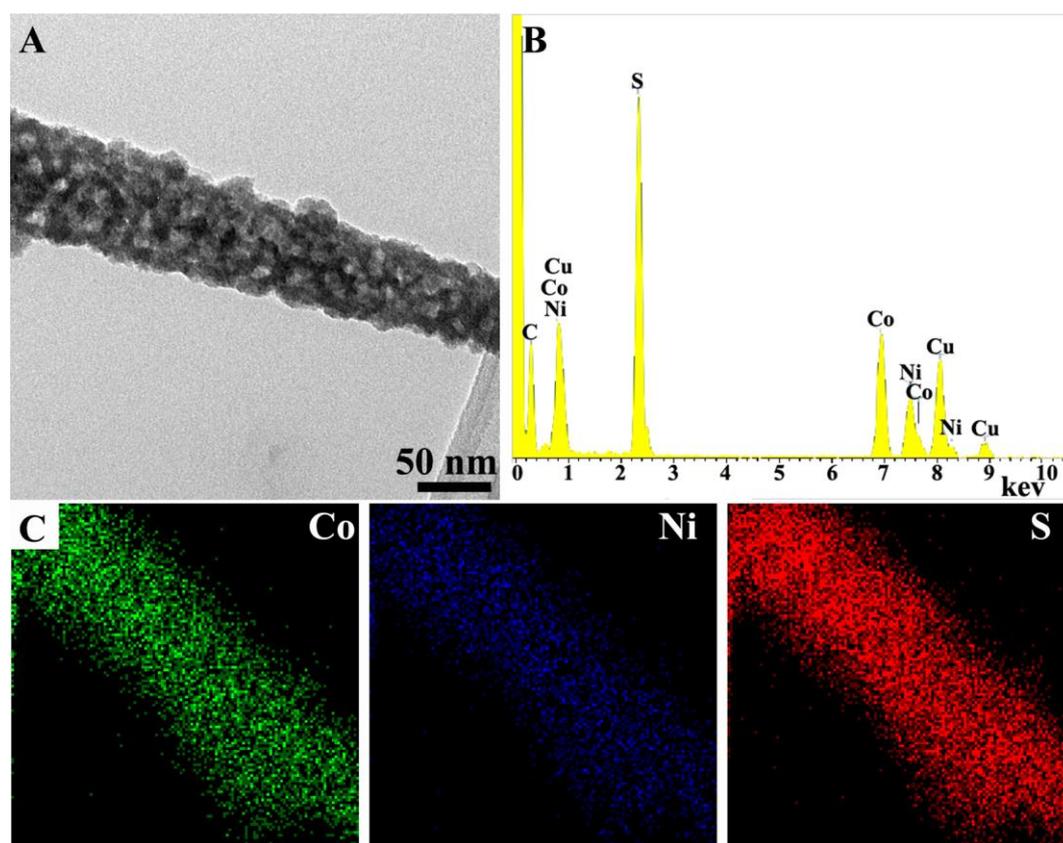


Figure SI-3. (A) TEM image and (B, C) EDX results of the NiCo_2S_4 nanorods transferred from the $(\text{Ni, Co})(\text{CO}_3)_{0.5}\text{OH}$ nanorod under H_2S atmosphere for more than 4 days. Cu and C elements come from Cu grid and carbon film on Cu grid. Co, Ni and S elements should be ascribed to NiCo_2S_4 . No O element is detected from EDX spectrum, indicating that the $(\text{Ni, Co})(\text{CO}_3)_{0.5}\text{OH}$ nanorod is fully reacted with H_2S to form NiCo_2S_4 .

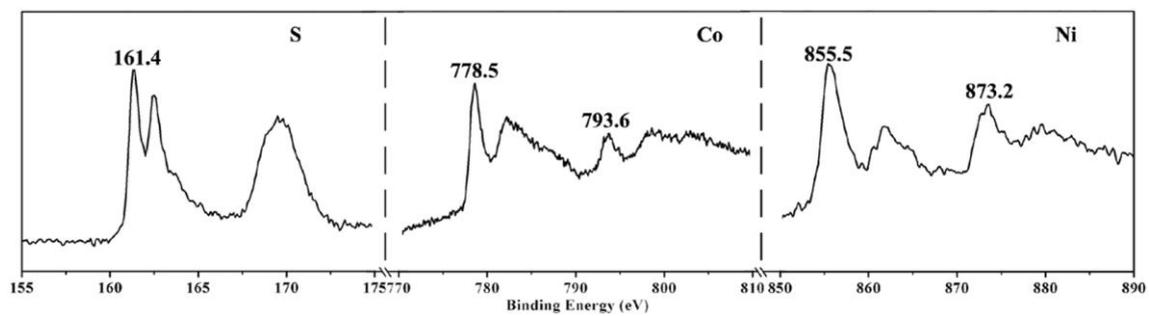


Figure SI-4. XPS spectra of the regional S 2p, Co 2p, and Ni 2p of hollow NiCo₂S₄ nanorod.

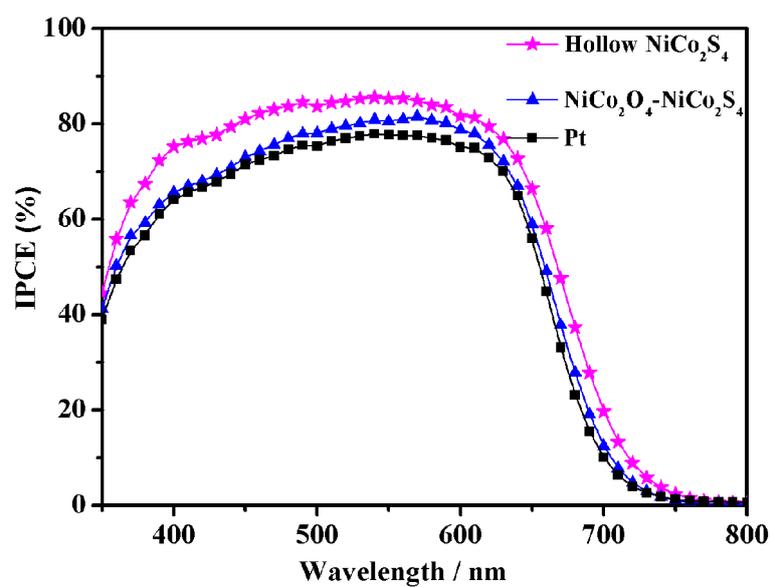


Figure SI-5. The incident photon-to-current conversion efficiency (IPCE) spectra of Pt, NiCo₂O₄-NiCo₂S₄, and hollow NiCo₂S₄ CEs based on QDSCs.

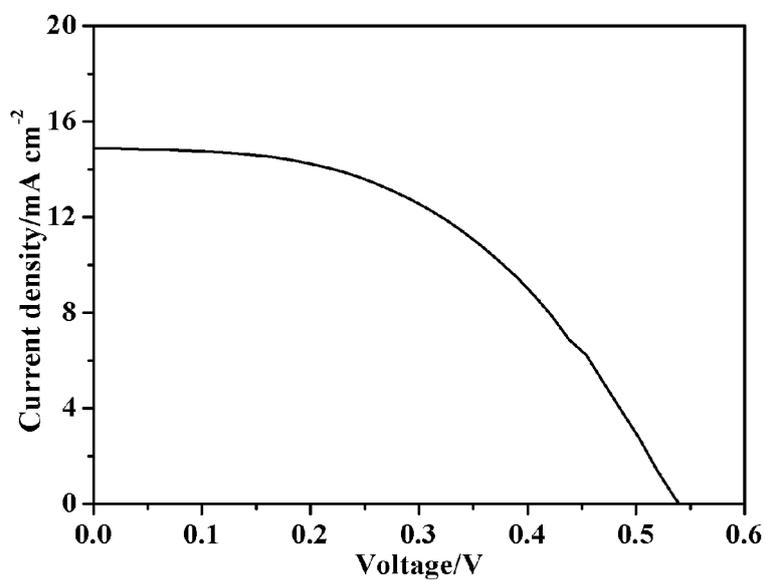


Figure SI-6. *J-V* characteristic curves of the QDSCs based on hollow NiCo₂S₄ nanorod CEs after being stored for 12 h.

1. V. Gonzalez-Pedro, X. Xu, I. Mora-Sero and J. Bisquert, *ACS Nano*, 2010, **4**, 5783-5790.
2. H. Lee, M. K. Wang, P. Chen, D. R. Gamelin, S. M. Zakeeruddin, M. Gratzel and M. K. Nazeeruddin, *Nano Lett.*, 2009, **9**, 4221-4227.